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Experimental Analysis Of Natural Refrigerant Blends For Household Application

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ABSTRACT

Hydrofluorocarbon (HFCs), due to their high global warming impact, are not considered a desirable solution for future household application. In accordance to the Kigali Amendment to the Montreal Protocol, numerous countries committed the significant phase-down of the production and consumption of HFCs over the next two to three decades. Natural refrigerants as well as their blends are considered viable alternatives due to their low global warming potentials. Additionally, the use of non-azeotropic refrigerant blends can positively influence the cycle performance of refrigerators and heat pump tumble dryers.

Moreover, the knowledge about the behaviour of the oil-refrigerant-mixture is a necessity to enable a more precise component design and dimensioning. While most pure refrigerants are experimentally well investigated, the properties of specific refrigerant blends and especially their oil-refrigerant-mixtures need to be measured.

This paper describes the initial experimental investigations of pure propane (R290) and pure iso-butane (R600a) in mixture with a mineral oil (MO). The presented results serve as basis for further investigations and conclusions regarding the ternary mixture, i.e. the refrigerant blend with the mineral oil. Several test benches were built to investigate the properties of interest, such as vapour pressure, viscosity as well as the density of the mixtures.

1. INTRODUCTION

Modern household appliances for cooling and heating should be robust, simple and cheap, have a long life time, low energy consumption and a low environmental impact. Therefore, most refrigerant cycles for household applications work with oil lubricated compressors and without an oil separator. A certain ratio of the lubricant is carried out the compressor and is, due to the missing oil separation, circulating through the refrigerant cycle. Depending on the pressure level and temperature a particular amount of refrigerant is dissolved in the oil and leads to changes of the thermophysical fluid properties of the mixed fluid. For the design of new cycles and their components for new refrigerant mixtures this change of fluid properties need to be observed. To substantiate design calculation models for the different components the fluid properties solubility, viscosity and density were experimentally determined at different pressure and temperature levels. The refrigerants iso-butane and propane were chosen because as pure refrigerants they are already used in many household and light commercial applications like refrigerators and heat pump tumble dryers. A zeotropic mixture of both refrigerants enables exergetic advantages at the heat transfer in the heat exchangers and in the whole cycle like shown in the experimental studies of Richardson and Butterworth (Richardson & Butterworth, 1995), Jung et al. (Jung, 2000), Mohanraj et al. (Mohanraj, 2009) and Agrawal et al. (Agrawal, 2017). In this paper the initial measurements of the pure refrigerants with a mineral oil are presented. For this experimental study a mineral oil with the viscosity group ISO VG10 was used. Since it can be assumed that the chemical structure of the lubricant (mineral oil) and the hydrocarbon refrigerants propane and iso-butane are similar, no mixing gaps within the selected measurement range were expected, which was validated with the solubility measurements.

2. THEORETICAL CONSIDERATIONS

This paper is based on measurements. However, for the analysis of the measured data equations of state (EOS) are used. These EOS were fit to the measured data points to allow for interpolation between the data points. For each presented fluid property various forms of EOS are known in literature. The correlated coefficients of the used EOS need to be adapted by the measured data points. This adaptation was done with the help of equation solver MATLAB.

2.1 Solubility Calculations

The solubility measurement provides basic information on the solubility of the lubricant in the refrigerant and the resulting vapour pressure of the mixture. Furthermore, its results are used for the analysis of the density and viscosity measurements. To determine the saturation pressure of the mixture the saturation pressure p_{sat} of pure refrigerant was approximated with the Antoine equation, at first.

$$P_{sat}(T) = A\,exp\left(-\frac{B}{T}\right) \tag{1}$$

Where T is the Temperature in Kelvin, and coefficients A and B can be determined through mathematical regression based on the measured vapour pressure data.

To determine the measured saturation pressure of the mixture as function of the temperature and the mass fraction of a lubricant a factor k can be added. This factor k is suggested by Cavestri (Cavestri, 1995).

$$p(T, \xi_{ref}) = \xi_{ref}\, p_{sat} k \tag{2}$$

$$k = 1 + \left(1 - \xi_{ref}\right)\left(a + b\frac{T}{T_{crit}} + c\left(\frac{T}{T_{crit}}\right)^2 + d\xi_{ref} + e\xi_{ref}\frac{T}{T_{crit}} + f\xi_{ref}\left(\frac{T}{T_{crit}}\right)^2\right) \tag{3}$$

The use of the mole fraction x_{ref} would be the natural basis from Raoult's law. However the molecular weight of the lubricant is typically a very uncertain value and often not known. Thus, the mass fraction ξ_{ref} of the refrigerant in kg kg^{-1} was used. T is the measured Temperature in K, T_{crit} the critical temperature of the refrigerant in K and a, b, c, d, e and f are coefficients determined based on the measured data. To get the temperature reduced to a dimensionless value it was divided by the critical temperature of the refrigerant. Furthermore, it is necessary for extrapolating the function to higher temperatures which is essential since the experimental temperature range is limited, see also section 3.

2.2 Boiling liquid density calculation

To determine the density of the refrigerant lubricant mixture equation (4) (Cavestri, 1995) can be used to fit the measured data.

$$\rho(T, \xi_{oil}) = a + b\,\xi_{oil} + c\,T + d\,\xi_{oil}\,T \tag{4}$$

T is the temperature in degree Celsius, ξ_{oil} is the mass fraction of the lubricant, ρ is the density of the mixture. Due to the polynomial form of the equation it cannot be used for extrapolations to temperatures higher or lower than the fitting limits.

2.3 Viscosity measurements

The kinematic viscosity of a refrigeration machine's lubricant is the most important parameter to describe the load-carrying capacity and the buildup of the lubricant film. For refrigeration oils, the kinematic viscosity is

$$\nu = \frac{\eta}{\rho} \tag{5}$$

Where η is the dynamic viscosity in mPa ·s and the ρ is the fluid density in kg m^{-3}. (Bock & Puhl, 2010).

To approximate the measured dynamic viscosity η as a function of the temperature T and mass fraction of the lubricant ξ_{oil} equation (6) can be used to fit the measured data. The fit equation is given by (Cavestri, 1995).

$$\eta(T, \xi_{oil}) = \exp(a + b\,T + c\,T^2 + d\,\xi_{oil} + e\,{\xi_{oil}}^2 + f\,\xi_{oil}\,T) \tag{6}$$

3. EXPERIMENTAL SETUP

Following section introduces the experimental setup of used test apparatuses for the investigations of properties that build the basic of this paper.

3.1 Solubility measurements

For measuring the solubility of the refrigerant in the oil the test apparatus shown in Figure 1 was used. The test tube made of borosilicate glass was filled with a refrigerant-lubricant mixture. The pressure of the vapour phase, the temperature of the liquid phase and the liquid level of the refrigerant-lubricant mixture were measured. The whole test apparatus was temperature conditioned in an environmental test chamber. To protect the measurements devices from breaking due to too high and too low temperatures, the temperature range was set from -35 °C to 80°C.The according pressure ranges up to 20 bar.

The mass fraction of the refrigerant in the lubricant in the liquid phase was varied from 10% to 90% refrigerant within the oil.

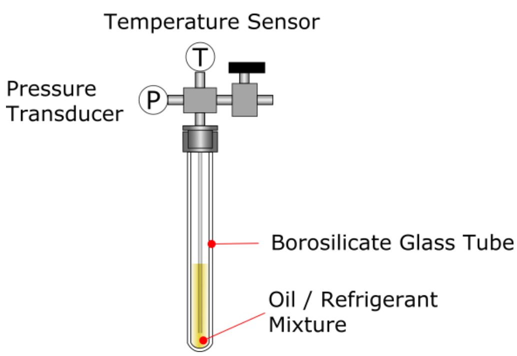

Figure 1: Test apparatus of solubility test.

3.2 Density and viscosity measurements

The liquid density of the oil is measured by an electrically oscillating U-tube density meter. While varying the frequency of the oscillation until the natural frequency is adjusted and the meter gives the value of the density in kg m^{-3}.

The viscosity of the refrigerant oil mixture is measured simultaneously to the density measurements by a viscometer. The viscometer is a massive body oscillation at a constant frequency. The meter measures the damping due to power losses and transfers the value of dynamic viscosity in Pa s

The density, as well as the viscosity measurements are carried out simultaneously in a pressurised test apparatus as outlined in Figure 2.

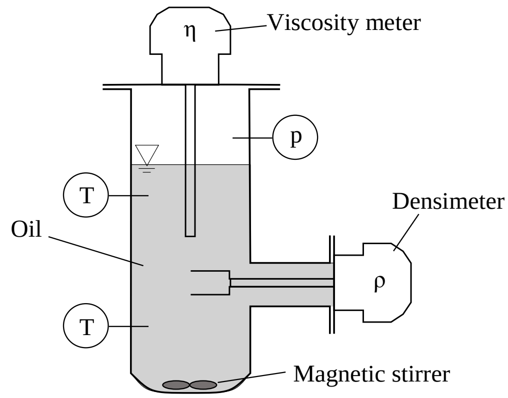

Figure 2: Test apparatus density and dynamic viscosity measurements

The well insulated apparatus consists of a pressure proof double- shell steel vessel which can be temperature controlled by circulating glycol in the double shell. The test apparatus enables temperatures measurement within the oil, the vapour pressure of the refrigerant, as well as the density and dynamic viscosity of the oil/ oil- refrigerant mixture. While varying the temperature from 75°C to 0°C the oil is kept in motion by a magnetic stirrer.

4. RESULTS

In consideration of the measured data and the EOS the V-p-T-diagrams were created. As mentioned before the saturation pressure measurement is a basic for the other introduced fluid properties. Therefore the influence of the lubricant of the saturation pressure is presented in a p-ξ_{Oil}-diagram for various temperatures first. The determined coefficients of the fit curves are listed in the tables above the diagrams.

4.1 Solubility measurements

Figure 3 displays the measured saturation pressures of the propane mineral oil mixture at different temperatures as well as the calculated trend line. The fitting was determined by equation (3) by means of the measured data and the equation solver MATLAB. The calculated coefficients are shown in Table 1.

Table 1: Coefficients of equation (1) and (3) for propane mineral oil mixture.

A	B	a	b	c	d	e	f
19364	2271.5	-0.7432	12.69	-9.982	2.994	-19.02	14.72

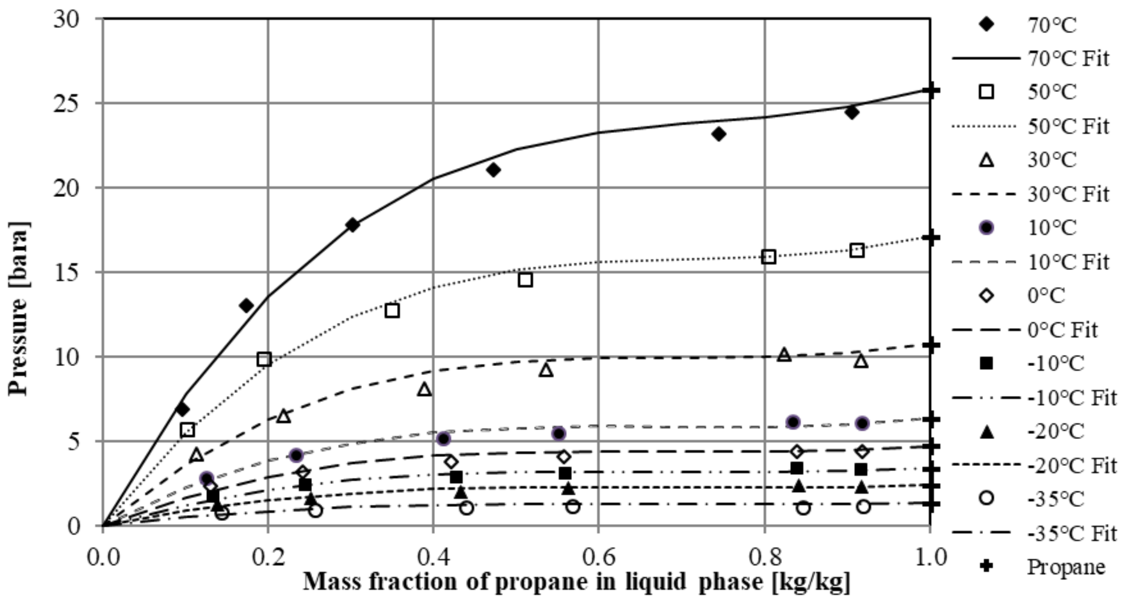

Figure 3: Saturation pressure as function of temperature and mass fraction of propane. The measured points are marked by dots.

For low temperatures the measurement data and the fit of equation (1) and (3) with the coefficients of table 1 fit well with a maximum deviation of 5%. For high temperatures, see the curves for 30°C to 70°C, the measurement data diverges more from the calculated line with a maximum deviation up to 10%. Here, the vapour- liquid equilibrium is more sensible to low temperature changes. It is still under investigation whether this is a thermodynamic effect, or a fragment produced by measurement inaccuracy.

The same measurements were done for a mixture of iso-butane and the same mineral oil. The calculated coefficients are shown in Table 2 and the pressure function in Figure 4.

Table 2: Coefficients of equation (1) and (3) for iso-butane mineral oil mixture

A	B	a	b	c	d	e	f
19832	2577	2.452	2.722	-3.691	-8.846	16.2	-9.052

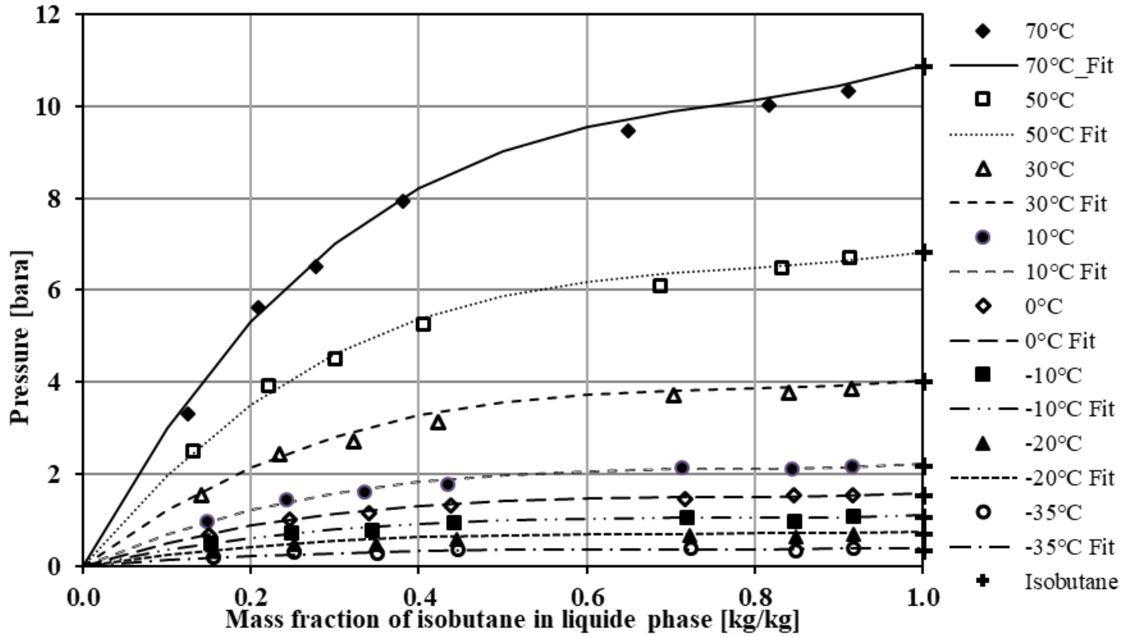

Figure 4: Saturation pressure as function of temperature and mass fraction of iso-butane. The measured points are marked by dots.

As it can been seen in Figure 4 the vapour pressure determined from above equation fit the experimental data very well with a maximum deviation of 5%.

4.2 V-p-T curves (Daniel plot)

For technical applications as for the design of important components of a refrigeration cycle like the compressor and heat exchangers the application of so-called Daniel-plots is common. The combination of vapour pressure and kinematic viscosity in the same diagram represents an easy way to determine a multitude of interesting properties based on pressure and temperature as variables.

The measured data was therefore used to determine the coefficients for equations (4) and (6) for both iso-butane and propane mixture data.

Table 3: Coefficients a to f of equation (4) for the mineral oil in mixture with propane and iso-butane

Refrigerant	a	b	c	d	e	f
Propane	-4.344	0.01621	0.0002161	9.257	-1.381	-0.06717
Iso-butane	-1.24	-0.04	0.00	9.55	-4.733	-0.0004115

Table 4: Coefficients a to d of equation (6) for the mineral oil in mixture with propane and iso-butane

Refrigerant	a	b	c	d
Propane	534.50	-1.77	319.30	1.20
Iso-butane	582.8	-1.342	266.4	0.6356

The determined density and dynamic viscosity data is then used to determine the kinematic viscosity of the mineral oil in mixture with the refrigerant by equation (5).

Following Figure 5 shows the Daniel-plot for the mineral- oil in mixture with propane and Figure 6 shows the same for mixtures with iso-butane.

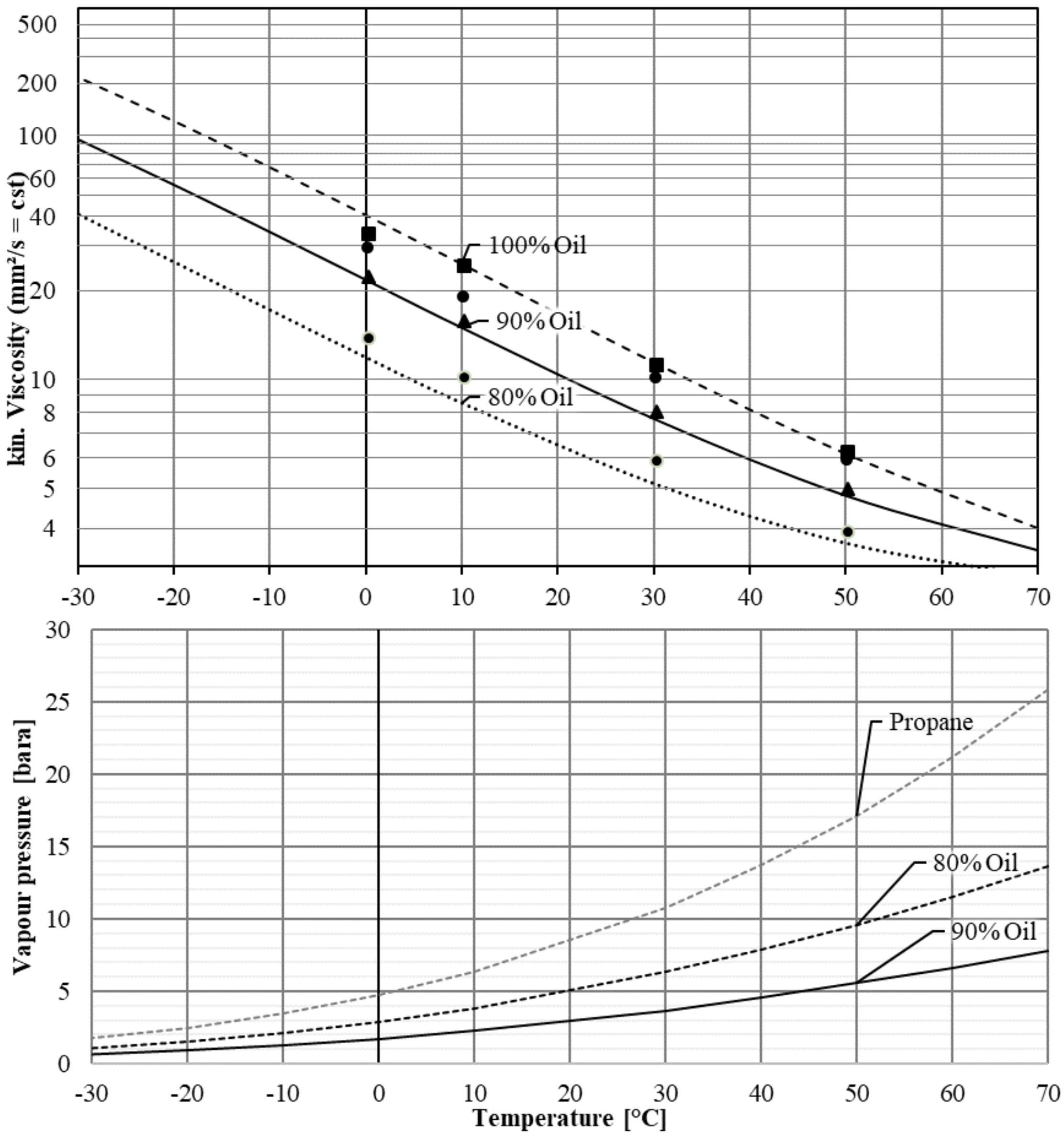

Figure 5: Vapour pressure and kinematic viscosity of the propane- mineral oil- mixture as function of temperature

The lines displayed show the determined fit curves for the vapour pressure and kinematic viscosity of the propane-mineral oil- mixture at essential mixing ratios used for compressor designing.

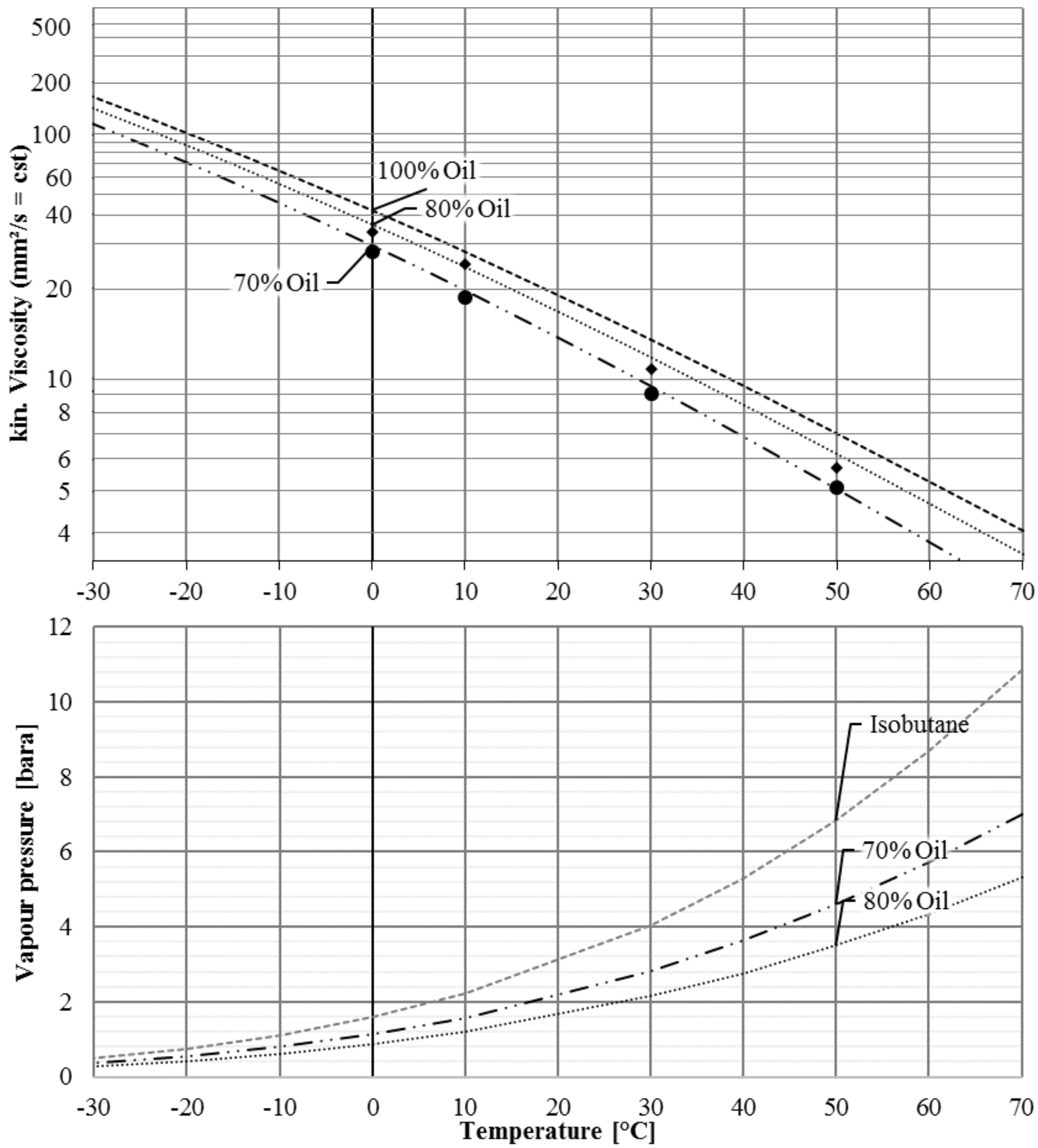

Figure 6: Vapour pressure and kinematic viscosity of the iso-butane- mineral oil- mixture as function of temperature

5. CONCLUSIONS

For both refrigerant- lubricant- mixtures, propane-MO and iso-butane-MO, the fluid properties were measured. These included the vapour pressure as function of the temperature and oil mass fraction and the density as well as the dynamic viscosity as function of the temperature and pressure. The data was then used to calculate the kinematic viscosity and to draw the V-p-T curves.

These basic measurements are necessary to combine the measurement results in order to draw inferences from the results of the binary mixtures about the ternary mixtures of iso-butane/propane with the mineral oil which are to be validated with measurements. These will be presented in future research paper.

NOMENCLATURE

Symbol	Meaning	Unit
p	pressure	bara
T	Temperature	°C
x	Mole fraction	mol mol^{-1}
ξ	Mass fraction	kg kg^{-1}
ρ	Density	kg m^{-3}
η	Dynamic viscosity	mPa s
ν	Kinematic viscosity	mm^2 s^{-1} ; cst

Subscript

crit	critical
ref	refrigerant
oil	oil

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